Jurnal Teknologi Industri Pertanian
26 (2):177-188 (2016)
ISSN 0216-3160 EISSN 2252-3901
Terakreditasi DIKTI No 56/DIKTI/Kep/2012

CHARACTERIZATION OF CELLULOSE FROM OIL PALM FROND (OPF) AND DISTILLED VETIVER ROOT (DVR) AND ITS APPLICATION AS POLYPROPYLENE COMPOSITE REINFORCEMENT

KARAKTERISASI SELULOSA DARI PELEPAH SAWIT DAN AMPAS AKAR WANGI SERTA APLIKASINYA UNTUK PENGUAT KOMPOSIT POLIPROPILENA

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Paper: Received 20 March 2015; Revised 22 September 2015; Accepted 30 November 2015

ABSTRAK

Sifat mekanis selulosa yang cukup tinggi memungkinkan selulosa digunakan sebagai penguat dalam komposit polipropilena. Dalam penelitian ini, selulosa diekstrak dari pelepah sawit dan ampas akar wangi melalui proses pulping dan pemucatan. Tujuan dari penelitian ini adalah mengetahui karakteristik selulosa dari pulp soda dan pulp pucat pelepah sawit dan ampas akar wangi berdasarkan alomorf, kristalinitas dan ukuran kristalitnya. Komposit polipropilena dibuat dengan cara mencampur pulp (10%), polipropilena (PP) dan maleic anhydride polypropylene (MAPP) menggunakan rheomix pada suhu 180℃, 60 rpm selama 25 menit. Campuran serat/PP/MAPP dikempa panas pada suhu 190℃, 1,5 MPa selama 2 menit. Sifat mekanis komposit diuji menggunakan universal testing machine (UTM). Pengaruh jenis pulp (pulp soda dan pulp pucat) dan bentuk pulp (pulp terurai dan pulp padat) terhadap sifat mekanis komposit diuji keragamannya dengan analisa statistik faktorial dalam rancangan acak lengkap. Sifat mekanis komposit PP/OPF lebih tinggi dibandingkan komposit PP/dVR. Keteguhan lentur komposit PP/OPF dipengaruhi oleh bentuk pulp, sedangkan keteguhan tarik komposit PP/OPF dipengaruhi oleh jenis pulp. Keteguhan lentur, modulus elastisitas lentur, keteguhan tarik dan modulus elastisitas tarik komposit PP/pulp-padat-pucat OPF berturut-turut 22.95%, 28.95%, 9.28% dan 56.53% lebih tinggi dibandingkan polipropilena tanpa pulp.

Kata kunci: ampas akarwangi, komposit, pelepah sawit, polipropilena, selulosa

ABSTRACT

Due to its mechanical properties, cellulose is potential to be utilized as reinforcement in polypropylene composite. In this study, cellulose was extracted from oil palm frond (OPF) and distilled vetiver root (dVR) by pulping and bleaching process. Soda pulp and bleached soda pulp of OPF and dVR were analysed based on their morphology, cellulose allomorph, cellulose crystallinity, and cellulose crystal size. Polypropylene composites were produced by mixing soda pulp or bleached soda pulp of OPF or dVR (10 wt%) with polypropylene (PP) and maleic anhydride polypropylene (MAPP). The mixing was conducted in rheomix at 180°C, 60 rpm for 25 min. Pulp/PP/MAPP compound was hot-pressed at 19°C, 1.5 MPa for 2 min. Composite mechanical properties were tested by universal testing machine (UTM). The effect of pulp type (soda pulp and bleached soda pulp) and pulp shape (fibrillated pulp and pressed pulp) on composite mechanical properties were statistically analysed based on analysis of variance. Mechanical properties of PP/OPF composites were higher than those of PP/dVR composites. PP/OPF composite flexural strength was influenced by pulp shape, whereas PP/OPF composite tensile strength was influenced by pulp type. The flexural strength, flexural modulus, tensile strength and tensile modulus of composite PP/pressed-bleached-pulp of OPF were 22.95%, 28.95%, 9.28% and 56.53% higher than neat polypropylene.

Keywords: cellulose, composite, distilled vetiver root, oil palm frond, polypropylene

PENDAHULUAN

The utilization of natural fibers as reinforcement in composite materials have attracted many researchers during the last decade. The advantages of natural fibers over synthetic fibers are low cost, low density, acceptable specific strength properties, ease of separation, and biodegrability (Mohanty *et al.*, 2002). Furthermore, natural fibers are renewable, non-abrasive to process equipment and can be incinerated at the end of their life cycle for energy recovery, because of their good calorific value (Pervaiz and Sain, 2003). Natural fiber-reinforced thermoplastics in automotive applications exhibit great potential due to some special characterizations over glass fiber composites. The natural fiber-reinforced thermoplastics composites have the combination characteristics of light weight

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(35–40% lighter than glass fiber), low-cost, better crash absorbance and sound insulation. Some potential applications in this field are door and instrument panels, package trays, glove boxes, arm rests, and seat backs (Pervaiz and Sain, 2003).

Among many kinds of thermoplastics, polypropylene (PP) and polyethylene (PE) are more suitable as matrix for natural fibers. PE, with melting point of 80 - 130°C (Sperling, 2006), and PP with melting point of 130 - 171°C (Shubhra *et al.*, 2011), are appropriate with the required-processing-temperature for fiber incorporation into polymer matrix. Taj *et al.* (2007) stated that the temperature for processing fiber-polymer composites should not exceed 230°C, due to the possibility of fiber degradation at above temperature (Mohanty *et al.*, 2000). Compare to PE, PP has several useful properties like heat distortion temperature, transparancy, flame resistance, dimensional stability and high impact strength which broaden its application. In addition, as a matrix, PP is widely used due to its excellent characters for composite fabrication. PP is also very suitable for filling, reinforcing and blending (Subhra *et al*., 2011).

Wood is the most common natural fiber resources and has been utilized as reinforcement in polypropylene matrix (Oksman and Clemons, 1997; Bledzki and Faruk, 2003; Bengtsson *et al.,* 2007; Lopez *et al.,* 2012). Due to wood supply depletation in relation to policy of wood utilization from forest plantation, the resource of natural fibers was extended to the utilization of non-wood natural fibers. For the reinforcement in polypropylene matrix, some of non-wood natural fibers have been used, such as kenaf, jute, hemp, flax, wheat, coir, oil palm empty fruit bunch (Zampaloni *et al*., 2007; Liu and Dai, 2007; Pickering *et al.*, 2007; Hornsby *et al.*, 1997; Gelfuso *et al*., 2011; Rozman *et al*,. 2003).

There are many factors that can influence the performance of natural fibers reinforced composites. The major drawbacks associated with the use of natural fibers in PP matrix are the poor wettability and weak interfacial bonding with PP. The hydrophilic cellulose fibers create a poor wettability as well as dispersability in the hydrophobic PP matrix (Subhra *et al.,* 2011). In nature, the elementary unit of a cellulose macromolecule is anhydro-d-glucose, which contains three hydroxyls (-OH). These hydroxyls form hydrogen bonds inside the macromolecule itself (intramolecular) and between other cellulose macromolecules (intermolecular) as well as with hydroxyl groups from moist air (Gassan and Bledzki, 1997). On the other hand, PP is nonpolar. In absance of polar groups on PP obstructs interfacial bonding between PP and natural fibers. To overcome these problems, chemical coupling agent, such as maleated PP (MAPP) was used. MAPP was produced by attaching polar groups (maleic anhydride) onto the molecular backbone of PP (Subhra *et al.,* 2011).

Apart from the hydrophilic nature of fiber, the properties of the natural fiber reinforced composites can also be influenced by origin or type of filler. It has been shown that fibers coming from the plant stems have different properties with respect to those taken from the leaves (Bisanda and Ansell, 1992).

In Indonesia, natural fiber resource that available in huge amount is oil palm frond (OPF). In a year, every hectar of oil palm plantation produced about 6 ton (dry weight) of oil palm frond (Supardjo, 2014), approximately. With oil palm plantation area of 10.46 million hectars in 2013 (Nuryati and Waryanto, 2014), there would be about 62.76 million tons OPF available per year. Another potential natural fiber resource is distilled vetiver root (dVR), by product from vetiver essential oil industry. The essential oil content in vetiver root was 0.4 - 0.5%. With vetiver plantation area of 2,330 Ha in Garut, West Java (central of vetiver producer) and productivity of 11–12 ton per Ha per year (Hobir 2005), there would be 25,527 ton dVR per year. The origin of those fiber are different. OPF fiber are originated from the upper part of plant, while dVR are from lower part of plant.

The main components of natural fibers are cellulose, hemicellulose and lignin. Due to its mechanical characteristics, cellulose is potentially functioned as reinforcement in plant cell wall. Futhermore, cellulose fibers can be utilized as reinforcing agent in polymer composite. Cellulose is isolated from natural fibers by a pulping process. Understanding cellulose characteristics from different part of plant (oil palm frond and vetiver root) could give more comprehensive knowledge in related to its utilization as reinforcement in composite product.

In polypropylene composite production, there are many kinds of technique to introduce cellulose fiber into polypropylene matrix. In this study, we analysed fibers of OPF or dVR soda pulp and bleached soda pulp based on their functional groups, morphology, cellulose allomorph, crystallinity, and crystal size. Futhermore, we have investigated the effect of pulp type (soda pulp or bleached pulp) and pulp shape (fibrillated pulp or pressed pulp) on composite mechanical properties.

MATERIALS AND METHOD

Materials and Equipments

Natural fibers used in this study were oil palm fronds, obtained from oil palm plantation in West Java, Indonesia and distilled vetiver roots, obtained from essential oil industry in Garut Regency, West Java, Indonesia. Sodium hydroxide at technical grade was used in pulping process. Bleaching process used technical grade of 50% hydrogen peroxide solution. Homopolymer polypropylene ($HI_{10}HO$) was supplied by PT Tri

Polyta Indonesia Tbk, with melt flow rate (MFR) of 10 g/10 min, density of 0.903 g/cm^3 and melting point of 163~173°C.

The equipments used in pulp preparation stage were ring flaker, digester and waterbath. Cellulose characterization was conducted by ABB FTIR MB3000, scanning electron microscope/ energy dispersive spectroscope (SEM/EDS) ZEISS EVO 50, Shimadzu XRD7000 MAXima X-ray diffractometer. Composite production used rheomix (HAAKE Polydrive) and hot press with maximum pressure of 350 kgf/cm^2. Mechanical properties of composite was conducted by universal testing machine (Shimadzu UTM AG-IS 50kN). The composite surface fracture was analyzed by optical microscope Dino-Lite.

Experiment Methods

Pulping and Bleaching

The oil palm frond (OPF) fibers were sun-dried and cut into ± 2 cm length. The moisture content of OPF fibers was 11.10%. To produce soda pulp, OPF fibers (500 g, dry basis) and NaOH solution with alkali active of 44.78% were put in digester with ratio of liquor-to-materials at 8:1. Pulping was conducted in 2 h and 46 min, at 176°C. After cooling of the digester, the pulp was collected and washed with water several times until neutralized.

The distilled vetiver root (dVR) were washed several times, sun-dried and cut into ± 2 cm length. The soda pulp of dVR fibers (moisture content of 8.59%) was produced by cooking dVR fibers (500 g dry basis) in digester with ratio of liquor-to-materials at 8:1. NaOH solution with alkali active of 35.95% was used to cook dVR fibers. Pulping was conducted in 3 h and 35 min, at 170°C. At the end of pulping process, the dVR soda pulp was collected and washed with water several times until neutralized.

The bleaching process was conducted in waterbath at temperature of 80°C. OPF or dVR soda pulp (20 g, dry basis), 300 mL of distilled water and 8 ml of hydrogen peroxide were added into 500 mL erlenmeyer and put in waterbath. Bleaching process was conducted in 4 cycles. In each cycle, 8 mL 50% hydrogen peroxide was added into erlenmeyer and heated at 80°C in waterbath for 1 h. After 4 h bleaching process, bleached pulp was collected and washed with water.

Charaterization of Pulp by Scanning Electron Microscopy

The morphology of soda pulp and bleached soda pulp were analysed by SEM/EDS ZEISS EVO 50, operated at 10 kV. Samples were coated with gold using a vacuum sputter-coater to improve conductivity of the samples and thus the quality of the SEM images.

Charaterization of Pulp by X-Ray Diffractometer

XRD measurements were performed on X-ray diffractometer XRD7000 MAXima to analyse cellulose crystallinity. The diffracted intensity of Cu Kα radiation (λ= 1.54 Å; 40.0 kV and 30.0 mA) was measured in a 2θ range between 10° and 40° with scan speed of 2.0 deg/min.

To determine crystallinity of cellulose (%), we used software to separate amorphous and crystalline contribution to the diffraction spectrum using a curve-fitting process of Lorentzian function. Crystallinity of cellulose (%) is calculated from the ratio of the area of all crystalline peaks (Icr) to the total area (Icr + Ia).

The atomic crystal size (Gumuskaya *et al.*, 2003) was calculated from the Scherrer equation (Eq. 1). This is a method based on the width of the diffraction pattern in the X-ray reflected crystalline region. In this study, the atomic crystal size were determined by using diffraction pattern obtaining from 101, 10-1, 002 and 040 lattice planes of samples.

$$D = \frac{k\lambda}{B\cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where D is the atomic crystal size (nm), k is the Scherrer constant (0.84), λ is x-ray wavelength (0.154 nm), B is the FWHM (full width at half maximum) of peak diffraction (rad) and θ (rad) is the corresponding Bragg angle.

Composite production

Filler for composite was varied based on pulp type (unbleached and bleached soda pulp) and pulp shape (fibrillated pulp and pressed pulp) from OPF and dVR. To prepare fibrillated pulp, soda pulp or bleached pulp of OPF or dVR were dried in oven at 105°C for 12 h. Next, dried pulp were milled in disc-mill. Meanwhile, we prepare pressed pulp of OPF or dVR soda pulp or bleached pulp. Kneading was conducted in a twin rotary mixer (rheomix) at 180°C, 60 rpm. As much as 47.14 g polypropylene was melting in rheomix for 6 min, then 2.36 g maleic anhydride grafted polypropylene (MAPP) were added into rheomix and melted for another 2 min. Then as much as 5.5 g pulp were added, and kneading process was continued for next 17 min. The compound of PP/OPF pulp or PP/dVR pulp were hot pressed into sheets at 190°C in two steps: pre-heating for 8 min and at pressure of 1.5 MPa for 2 min. Afterwards, sample was cooled at room temperature for another 5 min.

Mechanical Testing of PP-Composites

Composite flexural properties were examined based on ASTM D-790 “Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials”. The flexural specimens dimension were 60 x 10 x 1.5 mm. Five specimens of composites

were analysed using an UTM, at a cross-head speed of 1 mm/min and a lower support of 22 mm.

In addition composite tensile properties were also examined based on ASTM D-638 "Standard Test Method for Tensile Properties of Plastics". The width of narrow section of tensile "dumbell shape" specimens was 6 mm. Five specimens of composites were analysed using an UTM, at a cross-head speed of 2 mm/min and a gauge length of 25 mm.

Statistical Analysis

To analyze the effect of pulp type (soda pulp or bleached pulp) and pulp shape (fibrillated pulp or pressed pulp) on flexural and tensile properties of composite, the factorial design was applied. Each mechanical properties were carried out in five measurements. The variance between experiment treatments were analyzed using Minitab 16 statistical software in a 95% confidence level.

Composite's Surface Observation

The surface of composite before and after mechanical testing was analyzed by optical microscope with 200x magnification.

RESULT AND DISCUSSIONS

Morphology of Soda Pulp and Bleached Soda Pulp from Oil Palm Frond (OPF) and Distilled Vetiver Root (dVR)

Scanning electron microscope (SEM) images of soda pulp and bleached soda pulp from OPF and dVR are demonstrated in Figure 1. After pulping and bleaching process, OPF fibers were separated from lignocellulose of OPF cell wall (Fig. 1a and 1b). The fiber diameter in OPF soda pulp were varied from 4.78 - 12.41 µm. During bleaching, hydrogen peroxide removed residual lignin. Although there was a slightly difference in chemical composition between soda pulp and bleached pulp from OPF, the fiber length was not different. The fiber diameter in OPF bleached pulp were varied from 4.47 - 12.89 µm.

The SEM photograph shows that soda pulp of dVR was degraded more severe than OPF soda pulp, although dVR fibers were cooked with lower alkali concentration and lower temperature compare to OPF. After the distillation at temperature of 120°C for 16 h during vetiver oil extraction, dVR fibers were start to splits. Then pulping process that was conducted at temperature of 176°C, continued to disrupt lignocellulosic structure (Figure 1c). Fibers were split in the direction of fiber length and turned to be flattened fibers. Some fibers still remain in quite compact structure with diameter of 11.39 µm. While some others were flatten showing flat fibers with diameter of 20.98 µm.

In bleaching process, hydrogen peroxide removed residual lignin and reacted with non-lignocellulosic components. These reactions produced some materials that observed at the background of fibers (Figure 1d). There was flattened fiber observed and its diameter was 18.09 µm. After bleaching, dVR pulp was darker than OPF pulp (Figure 2).

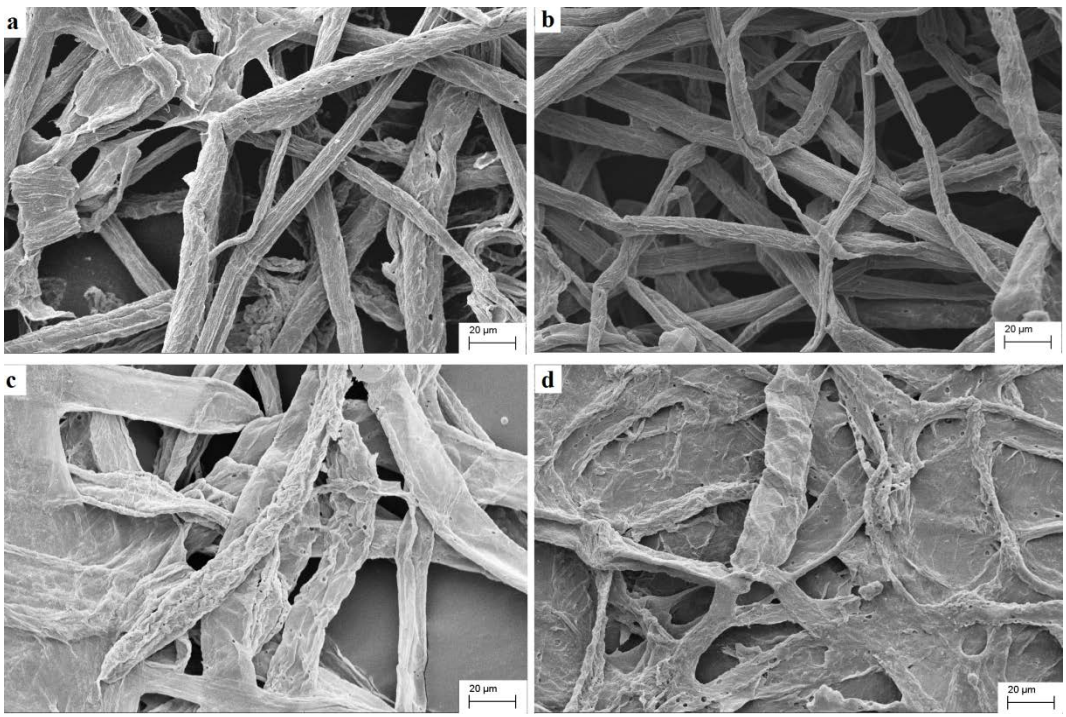


Figure 1. Soda pulp (a) and bleached soda pulp (b) of OPF, soda pulp (c) and bleached soda pulp (d) of dVR (500x mag).

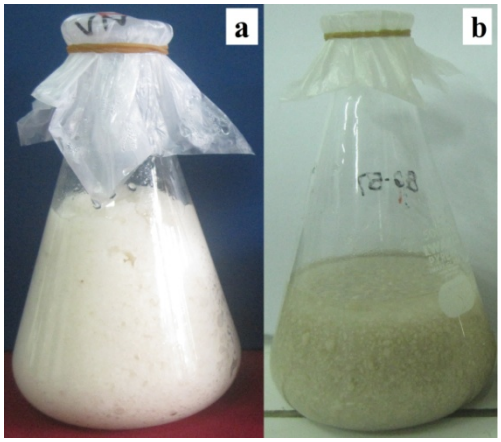


Figure 2. (a) OPF bleached pulp, (b) dVR bleached pulp

Cellulose Crystallinity of Soda Pulp and Bleached Soda Pulp from Oil Palm Frond and Distilled Vetiver Root

X-ray diffraction analysis was conducted to determine the crystallinity of cellulose. X-ray diffraction provides strong signals from the crystalline fraction of the cellulose. The X-ray diffractogram of OPF or dVR soda pulp and bleached pulp shows four peaks characteristic of cellulose I. Oudiani *et al.* (2011) proposed that the diffraction peaks for cellulose I from *Agave americana* L. fibers were located at 2θ = 14°, 16°, 23° and 35°, which were the positions of the (101), (10-1), (002) and (040), respectively. Whereas diffraction peaks for cellulose II from *A. americana* fibers treated with NaOH concentration of 30%, were located at 2θ = 11°, 20°, 22° and 37°.

In this study, the peaks of X ray signals from OPF soda pulp and bleached pulp, dVR soda pulp and bleached pulp, demonstrated the pattern of cellulose I (peaks at 2θ = 15°, 16°, 22° dan 34°). The peaks at 2θ = 20°, which was the positions of the (021) lattice plane of cellulose I, also appeared as shown in Table 1 and Figure 3. The soda pulping was conducted with NaOH at concentration of 5.60% for OPF and of 4.49% for dVR, as a result cellulose I was produced.

Oh *et al.* (2005) said that cellulose which was treated with 10 wt% NaOH at 25°C for 1 h and continued treated with 40 – 50 bar of CO_2 for 2 h, shows incomplete transformation of cellulose I to cellulose II. There were peaks at 2θ = 12.1°, 20.0°, 21.9° for cellulose II, which were the positions of the (101), (10-1) and (002), respectively. In addition, there were also peaks at 2θ = 14.7°, 16.8°, 20.5°, 22.7° for cellulose I. which were the positions of the (101), (10-1), (021) and (002), respectively.

Table 1. X ray diffraction peaks from sampels OPF and dVR

Samples	2θ angle of lattice plane (°)				
	101	10-1	021	002	040
Soda pulp OPF	15.0	15.7	20.7	22.5	34.2
Bleached pulp OPF	15.6	16.2	20.7	22.5	34.4
Soda pulp dVR	15.3	16.0	21.2	22.4	34.3
Bleached pulp dVR	15.2	17.0	20.6	22.4	34.4

The observed cellulose I allomorph in OPF and dVR pulp were cellulose Iβ which was a cotton-ramie type of cellulose (Table 2). Wada *et al.* (2001) has accomplished to estimate ratio of cellulose Iα/Iβ from the two equatorial d-spacings of crystal using discriminant analysis. The function used to discriminate between cellulose Iα and Iβ is presented as: Z = 1693d1 – 902d2 – 549, where Z>0 indicates the algal-bacterials (Iα-rich) type and Z<0 indicates the cotton-ramie (Iβ-dominant) type. In this study, d-spacings of crystal at lattice plane 101 and 10-1 were defined as d1 and d2, respectively.

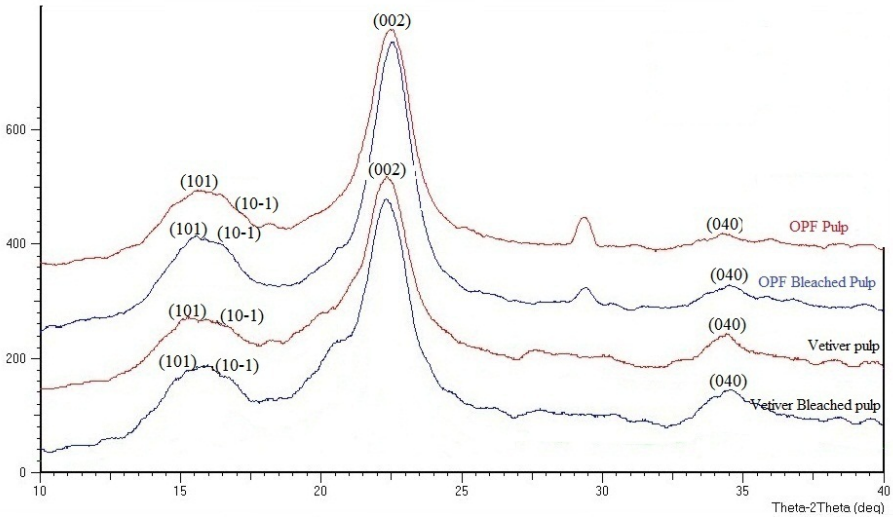


Figure 3. X ray diffractogram of soda pulp and bleached soda pulp from OPF and dVR

Table 2. The d-spacing of cellulose crystals

Samples	d spacing (nm)					Z	Cellulose type
	101	10-1	021	002	040		
Soda pulp OPF	0.589	0.565	0.428	0.395	0.262	-61.40	Iβ
Bleached pulp OPF	0.567	0.547	0.429	0.394	0.260	-82.54	Iβ
Soda pulp dVR	0.577	0.554	0.420	0.397	0.261	-71.85	Iβ
Bleached pulp dVR	0.582	0.522	0.430	0.397	0.260	-35.13	Iβ

Cellulose I, has a mix of two polymorphs; cellulose Iα which has a triclinic structure and celulose Iβ which has monoclinic structure with two cellulose chains per unit cell (Dri *et al.*, 2013). According to Ford *et al.* (2010), crystal d-spacing at 101, 10-1, 002 and 040 lattice plane in cellulose I were 0.601 nm, 0.535 nm, 0.394 nm and 0.258 nm, respectively. At this study, OPF and dVR pulp showed crystal d-spacing at 002 and 040 lattice plane of 0.39 nm and 0.26 nm, respectively. While the crystal d-spacing at 101 and 10-1 lattice plane were quite different from data from Ford *et al.* (2010), which were lower at 101 lattice plane and higher at 10-1 lattice plane.

Cellulose is semicrystalline polymer which composed of amorphous and crystalline fraction. The crystallinity of cellulose (Xc) is the ratio of crystalline index (Icr) and sum of amorphous index (Ia) and crystalline index (Icr). Soda pulp and bleached pulp of OPF, soda pulp and bleached pulp of dVR indicated crystallinity of 59.83%, 53.95%, 49.76% and 51.05%, respectively (Table 3). The crystallinity of soda pulp and bleached pulp of dVR were lower than of soda pulp and bleached pulp of OPF. These crystallinity values indicate that soda pulp and bleached pulp of dVR have more amorphous component compare to soda pulp and bleached pulp of OPF.

Table 3. Crystallinity of OPF and dVR samples

Samples	Crystalinity (Xc)		
	Crystalline (Icr)	Amorphous (Ia)	Xc (%)
Soda pulp OPF	1.141	0.766	59.83
Bleached pulp OPF	1.321	1.128	53.94
Soda pulp dVR	0.729	0.736	49.76
Bleached pulp dVR	0.839	0.804	51.05

The crystallinity of OPF soda pulp was higher than of OPF bleached pulp crystallinity. It was not common. Because, the purpose of bleaching with hydrogen peroxide was to degrade lignin (amorphous component) in soda pulp, through chemical oxidation of chromophore by the perhydroxyl anion from hydrogen peroxide decomposition. It appears that copper ion which was exist more than magnesium ion or calcium ion in OPF soda pulp caused the failure of bleaching agent to degrade lignin and tend to degrade carbohydrate instead.

In addition for measuring cellulose crystallinity, x- ray diffraction signals can be used to determine crystallographic parameters, like measuring the distances in the crystalline unit cell (Zugenmaier, 2001) or atomic crystal size (Nishiyama *et al.*, 2000). Atomic crystal size of cellulose in pulp samples (Table 4) was determined by using the diffraction pattern obtained from 101, 10-1, 002 and 040 lattice planes.

The strongest intensity, from the (002) plane, occur at the Bragg angle of 22.5° for OPF soda pulp dan bleached pulp and at Bragg angle of 22.4° for dVR soda pulp and bleached pulp (Figure 5). The crystallite size of samples at lattice plane (002) were 9.22 - 9.53 nm, and similar to crystallite size of wheat straw alpha cellulose, which was 9.1 nm (Gumuskaya and Usta, 2002). Derived from crystallite size data, pulping and bleaching of OPF and dVR have already successful to extract cellulose effectively.

Mechanical Properties of PP/OPF and PP/dVR Composites

Composite Flexural Properties

An analysis of variance (ANOVA) was used at $\alpha = 0.05$ to identify the effect of treatment on flexural properties. The flexural strength as a function of composite type is shown in Figure 4a. The flexural strength of OPF composites were higher than of dVR composites. The reinforcing capacity of cellulose fibers was influenced by the fiber dimension and orientation in composites (Bengtsson *et al.*, 2007). Based on SEM observation (Figure 1), mostly OPF fibers diameter were smaller than dVR fibers diameter. These smaller OPF fibers diameter presented higher fiber aspect ratio (length per diameter) and then gave the more reinforcing capacity in composites. Moreover, smaller fibers initiated a better fiber dispersion in polymer matrix due to improvement of interfacial adhesion between fiber and PP matrix.

It has been reported that the mechanical properties of polymer composites depend generally on the properties of the fiber, the properties of the matrix and the strength of the interfacial adhesion between them (Mallick, 1993). Strong and efficient interfacial adhesion is needed for the transfer of stress from the matrix to the fibers. In the same volume fiber fraction, the smaller fiber diameter lead to the more effective contact surface between fibers and PP compare to fiber with wider diameter.

Table 4. The atomic crystal size of OPF and dVR samples

Samples	FWHM (°)				2θ angle of lattice plane (°)				Atomic Crystal Size (nm)			
	101	10-1	002	040	101	10-1	002	040	101	10-1	002	040
Soda pulp OPF	1.360	2.680	1.640	0.853	15.0	15.7	20.7	22.5	11.00	5.59	9.22	18.18
Bleached pulp OPF	2.320	1.760	1.587	1.190	15.6	16.2	20.7	22.5	6.45	8.51	9.53	13.05
Soda pulp dVR	1.960	1.667	1.595	1.080	15.3	16.0	21.2	22.4	7.63	8.98	9.48	14.37
Bleached pulp dVR	1.560	0.560	1.623	1.320	15.2	17.0	20.6	22.4	9.59	26.77	9.31	11.76

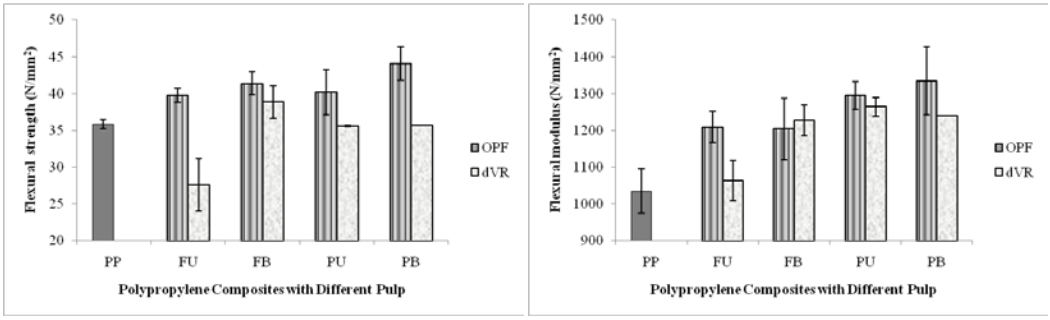


Figure 4. (a) Flexural strength and (b) flexural modulus of composite from PP with filler from pulp of OPF or dVR in form of fibrillated-unbleached (FU), fibrillated-bleached (FB), pressed-unbleached (PU), pressed-bleached (PB)

Based on analysis of variance, OPF composite's flexural strength was only influenced by pulp shape. The flexural strength of OPF composite made of pressed pulp (PU or PB) were higher than of fibrillated pulp (FU or FB). During pressed pulp production, drying process result in fibers entanglement due to the occurance of hydrogen bonding within pulp fibers. The melted polypropylene were covering entangled pulp fibers during the compounding process of pressed pulp OPF with polypropylene in rheomix and produced composite that could retained higher load.

The flexural strength of polypropylene was 35.85 N/mm^2. The addition of OPF pulp affected the PP/OPF composites flexural strength. The flexural strength of PP/OPF composites were 10.96% - 22.95% higher than of neat polypropylene. Similar to OPF composites, the flexural strength of dVR composites, was only influenced by pulp shape.

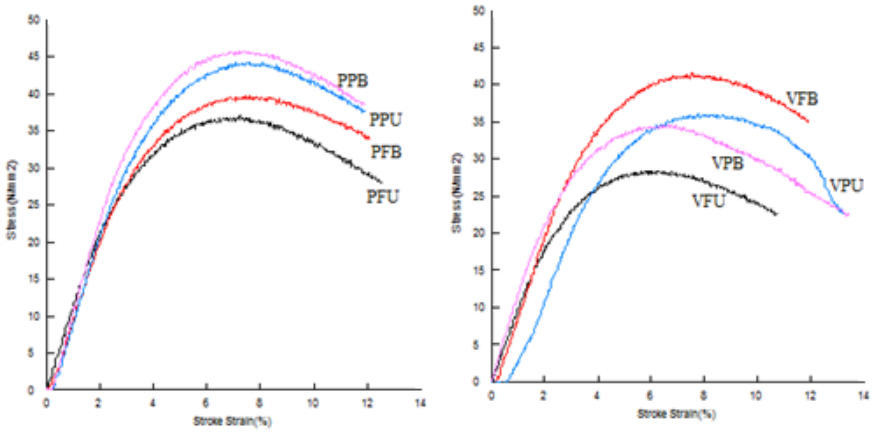
The flexural modulus as a function of composite type is shown in Figure 4b. Modulus (stiffness) is another basic mechanical property of composites. In general, fiber incorporation into matrix is usually increase the stiffness of the composite. The flexural modulus of polypropylene was 1035 N/mm^2. Due to pulp incorporation into PP, the flexural modulus of PP/dVR composites and PP/OPF composites increased to 2.77%-19.82% and 16.33% - 28.95% higher than neat polypropylene.

According to analysis of variance, OPF bleached pulp exhibited higher composite flexural modulus than soda pulp. Bleaching process had removed residual lignin and hemicellulose, produced cellulose fiber whose it's crystalline part performed as reinforcing agent. Crystalline part of cellulose fiber has orderly and dense structure compare to amorphous part. The existance of crystalline cellulose delivered higher composite flexural modulus.

The stress-strain graph of composites flexural properties were presented in Figure 5. Composite filled with bleached pulp could retained more stress than composite filled with unbleached soda pulp, when the flexural force was applied, and it agree with the composite flexural modulus.

Composite Tensile Properties

An analysis of variance (ANOVA) was used at $\alpha = 0.05$ to identify the effect of treatment on tensile properties. The tensile strength and tensile modulus as a function of composite type are shown in Figure 6a and 6b, respectively. Fibers give a significant influence on composite mechanical properties. The nature of fiber tensile strength affect the composite tensile strength directly. Based on previous study, OPF fibers tensile strength were 76.17 N/mm^2 while dVR fibers tensile strength were 30.12 N/mm^2 (Syamani *et al.*, 2013). When natural fibers were streched, such rearrangements among the fibrils would result in the better load sharing and hence result higher stress development in the fiber. And due to higher fiber tensile strength, OPF composites demonstrate higher tensile strength than dVR composites. Based on analysis of variance, tensile strength and tensile modulus of PP/OPF composites were not influenced, either by pulp type or pulp shape. Pulp type was influenced the tensile strength and tensile modulus of PP/dVR composites. However, PP/OPF composites demonstrate higher tensile properties than PP/dVR composites. The tensile strength of PP/pressed-bleached pulp of OPF was 24.59 N/mm^2 or 9.28% higher than of neat polypropylene.



(a) (b)

Figure 5. Stress-Strain graph of flexural properties of (a) PP/OPF composites (b) PP/dVR composites

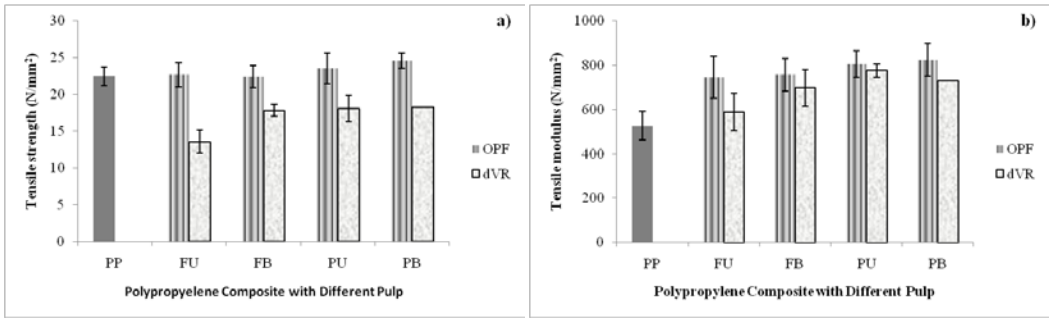


Figure 6. (a) Tensile strength and (b) tensile modulus of composite from PP with filler from pulp of OPF or dVR in form of fibrillated-unbleached (FU), fibrillated-bleached (FB), pressed-unbleached (PU), pressed-bleached (PB).

After pulping, as lignin is removed, the middle lamella joining the ultimate cell is expected to be more plastic as well as homogenous due to the gradual elimination of microvoids, while the ultimate cells themselves are effected slightly. And when the hemicellulose is removed after bleaching, the interfibrillar region is likely to be less dense and less rigid thereby makes the fibrils more capable of rearranging themselves along the direction of tensile deformation (Khalid *et al.*, 2008).

The polypropylene tensile modulus was 1140 N/mm^2. The addition of OPF pulp into PP, produced PP/OPF composites with tensile modulus of 1336 – 1488 N/mm^2. Whereas dVR pulp caused the increment of PP/dVR composite tensile modulus to become 1127 –1348 N/mm^2.

The stress-strain graph of composites tensile properties were demonstrated in Figure 7. Composite filled with OPF pulp could retained more stress than composite filled with dVR pulp, when experienced the tensile force. The higher tensile properties of OPF composite was influenced by filler properties that OPF fibers has higher tensile properties than of dVR fibers.

Cross Sectional Surface of Composites

Figure 8 and 9 show optical micrograph of the composite surfaces before and after tensile testing. The dispersion and distribution of the OPF or dVR pulp fibers within the polypropylene were studied. All of the OPF composites show that pulp fibers were more homogenous distributed in PP matrix, compare to dVR composites (Figure 8).

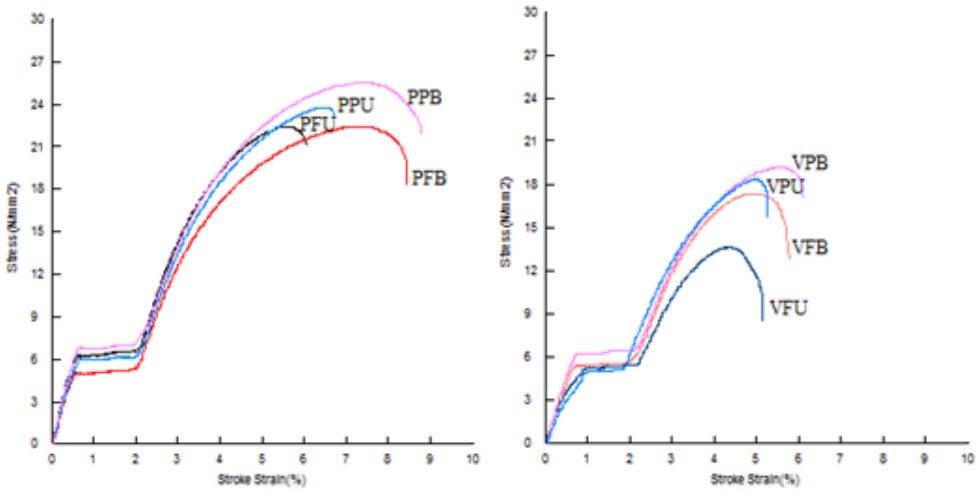
In PP/OPF composites, polypropylene was melted and covering OPF pulp, seen as white line in composite. Whereas, in PP/dVR composites, melted polypropylene were covering entangled pulp fibers (seen in circle) during the compounding process of pulp and polypropylene.

When soda unbleached pulp of OPF was compounding with PP (Figure 8a and 8b), they produce darker color composite compare to bleached pulp of OPF (Fig 8c and 8d). Meanwhile, the color of dVR composites from soda pulp or bleached pulp (Figure 8e, 8f, 8g, 8h) show no significant difference. Generally, soda pulping removed lignin from lignocellulosic materials. Lignin content in OPF or dVR were 20.76%, 39.53%, respectively (Syamani *et al.*, 2013). After soda pulping, residual lignin in OPF or dVR soda pulp were 6.05%, 5.10%, respectively. These residual lignin gave the brown color in soda pulp. In term of composite from bleached pulp of dVR, the composite color was darker than of composite from bleached pulp of OPF. According EDX analysis, different from OPF, soda pulp and bleached pulp of dVR contained iron.

Transition-metal ions and especially iron have been shown to form strongly coloured complexes with lignin and extractives and therefore contribute to the darkening of mechanical-pulp sheets (Forsskåhl, 2000; Yoon *et al.*, 1999). Both Fe^{3+} ions and Fe^{2+} ions can produce colour in pulp, either by forming complexes with phenols or by hydrolysing to form hydroxides (Gupta, 1970).

The cross sectional tensile-tested fracture surfaces of PP/OPF pulp composites were depicted in Figure 9a–9d. As is visible in the overview, OPF pulp fibers in form of fibrillated-pulp (Figure 9a and 9c) or pressed-pulp (Figure 9b and 9d) were easily visible as they agglomerated at several spot in polypropylene matrix (seen in circle). The OPF pulp fibers were not distributed evenly in polypropylene matrix. OPF fibrillated pulp were produced by milling in discmill without any further process, cutting or screening. While the dimension of OPF pressed-pulp that were introduced into rheomix, were 10 x 10 mm^2. Those pulp fibers dimension were not small enough that adhere pulp fibers dispersion in polypropylene matrix, thus the reinforcing capacity of pulp fibers were not efficient.

Although pulp fibers were not distributed evenly, there were almost no signs of fiber pull outs in OPF composites, especially in PP/OPF-bleached-fibrillated-pulp (Figure 9c) or PP/OPF-bleached-pressed-pulp (Figure 9d). The polypropylene could covered pulp fibers sufficiently with MAPP assistance as coupling agent thus improve interfacial bonding between fibers and polypropylene.



(a) (b)

Figure 7. Stress-Strain graph of tensile properties of (a) PP/OPF composites (b) PP/dVR composites

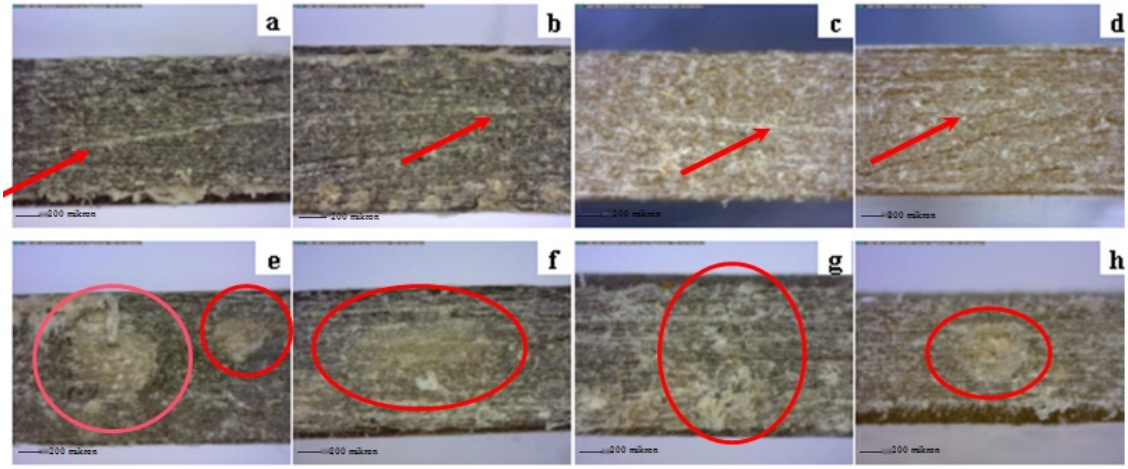


Figure 8. Micrograph of cross sectional surface before mechanical testing of (a) PP/OPF-unbleached-fibrillated-pulp, (b) PP/OPF-unbleached-pressed-pulp, (c) PP/OPF-bleached-fibrillated-pulp, (d) PP/OPF-bleached-pressed-pulp, (e) PP/dVR-unbleached-fibrillated-pulp, (f) PP/dVR-unbleached-pressed-pulp, (g) PP/dVR-bleached-fibrillated-pulp, (h) PP/dVR-bleached-pressed-pulp composites

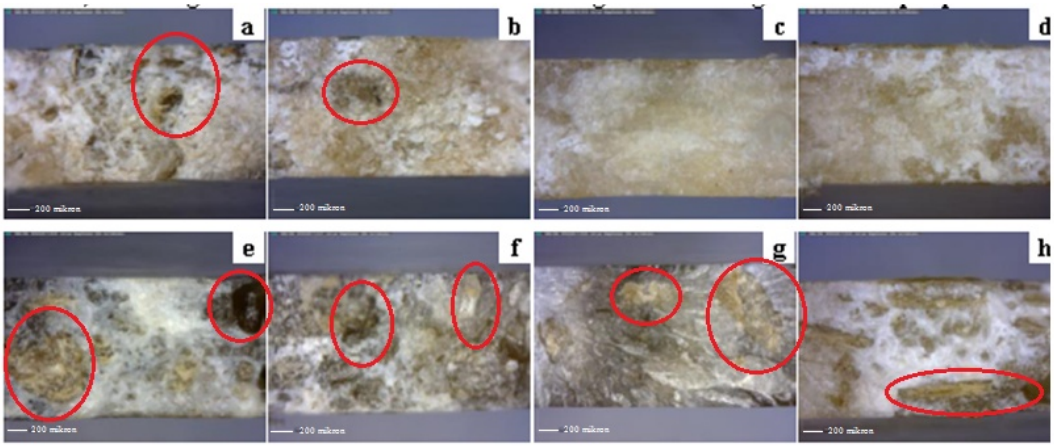


Figure 9. Micrograph of tensile-tested fracture surface of (a) PP/OPF-unbleached-fibrillated-pulp, (b) PP/OPF-unbleached-pressed-pulp, (c) PP/OPF-bleached-fibrillated-pulp, (d) PP/OPF-bleached-pressed-pulp (e) PP/dVR-unbleached-fibrillated-pulp, (f) PP/dVR-unbleached-pressed-pulp, (g) PP/dVR-bleached-fibrillated-pulp, (h) PP/dVR-bleached-pressed-pulp composites

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

After pulping and bleaching process, OPF fiber's diameter were not different significantly. Whereas dVR bleached pulp fiber's diameter were wider, compare to dVR soda pulp fiber's because the fibers were splitting in the direction of fiber's length. Soda pulp and bleached soda pulp of dVR crystallinity were lower than of OPF crystallinity. Soda pulp and bleached soda pulp of OPF and dVR have same cellulose allomorph which were cellulose Iβ with the crystallite size were 9.22 ~ 9.53 nm. The soda pulping at low concentration of NaOH produced cellulose I of OPF or dVR pulp. Mechanical properties of PP/OPF composites were higher than of PP/dVR composites. Composite flexural strength was influenced by pulp shape, whereas composite tensile strength was influenced by pulp type. The flexural strength, flexural modulus, tensile strength and tensile modulus of composite PP/pressed-bleached-pulp of OPF were 22.95%, 28.95%, 9.28% dan 56.53% higher than of neat polypropylene.

Recommendation

In this study, the cellulose content in composite was 10% of composite weight. To produce composite with higher mechanical properties, it is necessary to increase cellulose loading in the composite. And it is interesting to find out the comparison between using cellulose from kraft pulping method or soda pulping method, on composite characteristics.

ACKNOWLEDGEMENT

This research was part of first author's doctoral research and financially supported by Ministry of Research and Technology of Indonesia (Kemenristek) and Indonesia Endowment Fund for Education (LPDP).

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